

# THERMAL PROPERTIES AND PROCESSES

**D Hillel**, Columbia University, New York, NY, USA

© 2005, Elsevier Ltd. All Rights Reserved.

## Introduction

The soil temperature, as it varies in time and space, is a factor of primary importance in determining the rates and directions of soil physical processes and of energy and mass exchange with the atmosphere. Temperature governs evaporation and aeration, as well as the types and rates of chemical reactions that take place in the soil. Finally, soil temperature strongly influences biological processes such as seed germination, seedling emergence and growth, root development, and microbial activity.

Soil temperature varies in response to changes in the radiant, thermal, and latent energy exchange processes that take place primarily through the soil surface. The effects of these phenomena are propagated into the soil profile via a complex series of transport processes, the rates of which are affected by time-variable and space-variable soil properties.

## Modes of Energy Transfer

In general, there are three principal modes of energy transfer: radiation, convection, and conduction. By radiation, we refer to the emission of energy in the form of electromagnetic waves from all bodies above 0 K. According to the Stefan–Boltzmann law, the total energy emitted by a body,  $J_t$ , integrated over all wavelengths, is proportional to the fourth power of the absolute temperature  $T$  of the body's surface. This law is usually formulated:

$$J_t = \epsilon \sigma T^4 \quad [1]$$

where  $\sigma$  is a constant and  $\epsilon$  is the emissivity coefficient, which equals unity for a perfect emitter (generally called a 'black body'). The absolute temperature also determines the wavelength distribution of the emitted energy. The Wien law states that the wavelength of maximal radiation intensity  $\lambda_m$  is inversely proportional to the absolute temperature:

$$\lambda_m = 2900/T \quad [2]$$

where  $\lambda_m$  is in micrometers. The actual intensity distribution as a function of wavelength and temperature is given by Planck's law:

$$E_\lambda = C_1/\lambda^5 [\exp(C_2/\lambda T) - 1] \quad [3]$$

where  $E_\lambda$  is energy flux emitted in a given wavelength range and  $C_1$  and  $C_2$  are constants.

Since the temperature of the soil surface is generally of the order of 300 K (though it can range from below 273 K, the freezing point, to 330 K or higher), the radiation emitted by the soil surface has its peak intensity at a wavelength of approximately  $10 \mu\text{m}$  and its wavelength distribution over the range of  $3\text{--}50 \mu\text{m}$ . This is in the realm of infrared, or heat, radiation.

A very different spectrum is emitted by the sun, which acts as a black body at an effective surface temperature of approximately 6000 K. The sun's radiation includes the visible light range of  $0.3\text{--}0.7 \mu\text{m}$ , as well as some infrared radiation of greater wavelength (up to approx.  $3 \mu\text{m}$ ) and some ultraviolet radiation ( $\lambda < 0.3 \mu\text{m}$ ). Since there is very little overlap between the two spectra, it is customary to distinguish between them by calling the incoming solar spectrum 'short-wave' radiation, and the spectrum emitted by the Earth 'long-wave' radiation.

The second mode of energy transfer, called 'convection,' involves the movement of a heat-carrying mass, as in the case of ocean currents or atmospheric winds. An example more pertinent to soil physics would be the infiltration of warm waste water (from, e.g., a power plant) into an initially cold soil.

Conduction, the third mode of energy transfer, is the propagation of heat within a body by internal molecular motion. Since temperature is an expression of the kinetic energy of a body's molecules, the existence of a temperature difference within a body will normally cause the transfer of kinetic energy by the numerous collisions of rapidly moving molecules from the warmer region of the body to their neighbors in the colder region. The process of heat conduction is thus analogous to diffusion and, in the same way that diffusion tends in time to equilibrate a mixture's composition throughout, heat conduction tends to equilibrate a body's internal distribution of molecular kinetic energy – that is, its temperature.

In addition to the three modes of energy transfer described, there is a composite phenomenon which one may recognize as a fourth mode, namely latent heat transfer. A prime example is the process of distillation, which includes the heat-absorbing stage of evaporation, followed by the convective or diffusive movement of the vapor, and ending with the heat-releasing stage of condensation. A similar catenary process can also occur in transition back and forth

from ice to liquid water in soils subject to freezing and thawing.

### Energy Balance for a Bare Soil

The radiation balance of a bare soil surface can be written:

$$J_n = (J_s + J_a)(1 - \alpha) + J_{li} - J_{lo} \quad [4]$$

Here  $J_n$  is the net radiation, that is, the sum of all incoming-minus-outgoing radiant energy fluxes;  $J_s$  the incoming flux of short-wave radiation directly from the sun and  $J_a$  the short-wave diffuse radiation from the atmosphere (sky);  $J_{li}$  the incoming long-wave radiation flux from the sky and  $J_{lo}$  the outgoing long-wave radiation emitted by the soil; and, finally,  $\alpha$  is the albedo, or reflectivity coefficient, which is the fraction of incoming short-wave radiation reflected by the soil surface rather than absorbed by it. In the present context, all terms that do not pertain to the soil, namely  $J_s$ ,  $J_a$ , and  $J_{li}$ , are disregarded.

The albedo  $\alpha$  is an important characteristic of soil surfaces, and it can vary widely in the range of 0.1–0.4, depending upon the soil's basic color (whether dark or light), the surface's roughness, and the inclination of the incident radiation relative to the surface. In the short term, the albedo also depends on the changing wetness of the exposed soil. The drier the soil, the smoother its surface, and the brighter its color, the higher its albedo. To a certain extent, the albedo can be modified by various surface treatments such as tillage and mulching.

Apart from the reflected short-wave radiation, the soil also emits long-wave radiation. In accordance with eqn [1], the emitted flux  $J_{lo}$  depends primarily on soil surface temperature but is also affected by the soil's emissivity. This parameter, in turn, depends on soil wetness, but its range of variation is generally small, i.e., between 0.9 and 1.0.

The net radiation received by the soil surface is transformed into heat, which warms the soil and air and vaporizes water. We can write the surface energy balance as follows:

$$J_n = S + A + LE \quad [5]$$

where  $S$  is the soil heat flux (the rate at which heat is transferred from the surface downward into the soil profile),  $A$  is the 'sensible' heat flux transmitted from the surface to the air above, and  $LE$  is the evaporative heat flux, a product of the evaporative rate  $E$  and the latent heat per unit quantity of water evaporated,  $L$ .

The total surface energy balance (combining eqns [4] and [5]) is therefore:

$$(J_s + J_a)(1 - \alpha) + J_{li} - J_{lo} - S - A - LE = 0 \quad [6]$$

Conventionally, all components of the energy balance are taken as positive if directed toward the surface, and negative otherwise.

### Conduction of Heat in Soil

The conduction of heat in solid bodies was analyzed as long ago as 1822 by Fourier, whose name is associated with the linear transport equations that have been used ever since to describe heat conduction. The first law of heat conduction, known as the Fourier law, states that the flux of heat in a homogeneous body is in the direction of, and proportional to, the temperature gradient:

$$q_h = -\kappa \nabla T \quad [7]$$

Here  $q_h$  is the thermal flux (i.e., the amount of heat conducted across a unit cross-sectional area in unit time),  $\kappa$  is thermal conductivity, and  $\nabla T$  the spatial gradient of temperature  $T$ . In one-dimensional form, this law is written:

$$q_h = -\kappa_x \partial T / \partial x \quad \text{or} \quad q_h = -\kappa_z \partial T / \partial z \quad [8]$$

Here  $\partial T / \partial x$  is the temperature gradient in any arbitrary direction designated  $x$ , and  $\partial T / \partial z$  is, specifically, the gradient in the vertical direction representing soil depth ( $z=0$  being the soil surface). The subscripts attached to the thermal conductivity term are meant to account for the possibility that this parameter may have different values in different directions (i.e., that it may be nonisotropic). The negative sign in these equations is due to the fact that heat flows from a higher to a lower temperature (i.e., in the direction of, and in proportion to, a negative temperature gradient).

Equation [7] is sufficient to describe heat conduction under steady-state conditions, that is, where the temperature at each point in the conducting medium is invariant and the flux is constant in time and space. To account for nonsteady (transient) conditions, we need a second law analogous to Fick's second law of diffusion. To obtain the second law of heat conduction, the principle of energy conservation in the form of the continuity equation is invoked, which states that, in the absence of any sources or sinks of heat, the time rate of change in heat content of a volume element of the conducting medium must equal the change of flux with distance:

$$\rho c_m \partial T / \partial t = -\nabla \cdot q_h \quad [9]$$

where  $\rho$  is mass density and  $c_m$  specific heat capacity per unit mass (called simply 'specific heat' and

defined as the change in heat content of a unit mass of the body per unit change in temperature). The product  $\rho c_m$  (often designated  $C$ ) is the specific heat capacity per unit volume, and  $\partial T/\partial t$  is the time rate of temperature change. Note that  $\rho$  represents the total mass per unit volume, including the mass of water in the case of a moist soil. The symbol  $\nabla$  ('del') is the shorthand representation of the three-dimensional gradient. An equivalent form of eqn [9] is:

$$\rho c_m \partial T / \partial t = -(\partial q_x / \partial x + \partial q_y / \partial y + \partial q_z / \partial z)$$

where  $x, y, z$  are the orthogonal direction coordinates.

Combining eqn [9] with [7] gives the second law of heat conduction:

$$\rho c_m \partial T / \partial t = -\nabla \cdot (\kappa \nabla T) \quad [10]$$

which, in one-dimensional form, is:

$$\rho c_m \partial T / \partial t = \partial / \partial x (\kappa \partial T / \partial x) \quad [11]$$

Sometimes there is need to account for the possible occurrence of heat sources or sinks in the realm where heat flow takes place. Heat sources include such phenomena as organic matter decomposition, wetting of initially dry soil material, and condensation of water vapor. Heat sinks are generally associated with evaporation. Combining all these sources and sinks into a single term  $S$ , we can rewrite the last equation:

$$\rho c_m \partial T / \partial t = \partial / \partial x (\kappa \partial T / \partial x) \pm S(x, t) \quad [12]$$

in which the source-sink term is shown as a function of both space and time.

## Volumetric Heat Capacity of Soils

The volumetric heat capacity  $C$  of a soil is defined as the change in heat content of a unit bulk volume of soil per unit change in temperature. Its units are calories per cubic centimeter per degree (Kelvin) or joules per cubic meter per degree. As such,  $C$  depends on the composition of the solid phase (mineral and organic constituents) of the soil, on bulk density, and on soil wetness (Table 1).

The value of  $C$  can be estimated by summing the heat capacities of the various constituents, weighted according to their volume fractions:

$$C = \sum f_{si} C_{si} + f_w C_w + f_a C_a \quad [13]$$

Here,  $f$  denotes the volume fraction of each phase: solid (subscripted 's'), water ('w'), and air ('a'). The solid phase includes a number of components subscripted 'i,' such as various minerals and organic

**Table 1** Densities and volumetric heat capacities of soil constituents (at 10°C) and of ice (at 0°C)

Constituent	Density $\rho$		Heat capacity $C$	
	$\text{g cm}^{-3}$	$\text{kg m}^{-3}$	$\text{cal cm}^{-3} \text{K}$	$\text{J m}^{-3} \text{K}$
Quartz	2.66	$2.66 \times 10^3$	0.48	$2.0 \times 10^6$
Other minerals (mean)	2.65	$2.65 \times 10^3$	0.48	$2.0 \times 10^6$
Organic matter	1.3	$1.3 \times 10^3$	0.6	$2.5 \times 10^6$
Water (liquid)	1.0	$1.0 \times 10^3$	1.0	$4.2 \times 10^6$
Ice	0.92	$0.92 \times 10^3$	0.45	$1.9 \times 10^6$
Air	0.00125	1.25	0.003	$1.25 \times 10^3$

Reproduced with permission from Hillel D (1998) *Environmental Soil Physics*. San Diego, CA: Academic Press.

matter, and the symbol  $\Sigma$  indicates the summation of the products of their respective volume fractions and heat capacities. The  $C$  value for water, air, and each component of the solid phase is the product of the particular density and the specific heat per unit mass (i.e.,  $C_w = \rho_w c_{mw}$ ;  $C_a = \rho_a c_{ma}$ ;  $C_{si} = \rho_{si} c_{msi}$ ).

Most of the minerals composing soils have nearly the same values of density (approx.  $2.65 \text{ g cm}^{-3}$  or  $2.65 \times 10^3 \text{ kg m}^{-3}$ ) and of heat capacity ( $0.48 \text{ cal cm}^{-3} \text{K}$  or  $2.0 \times 10^6 \text{ J m}^{-3} \text{K}$ ). Since it is difficult to separate the different kinds of organic matter present in soils, it is tempting to group them all into a single constituent (with mean density of approximately  $1.3 \text{ g cm}^{-3}$  or  $1.3 \times 10^3 \text{ kg m}^{-3}$ , and a mean heat capacity of approximately  $0.6 \text{ cal cm}^{-3} \text{K}$  or  $2.5 \times 10^6 \text{ J m}^{-3} \text{K}$ ).

The density of water is less than half that of mineral matter (approx.  $1 \text{ g cm}^{-3}$  or  $1.0 \times 10^3 \text{ kg m}^{-3}$ ); its specific heat is more than twice as large ( $1 \text{ cal cm}^{-3} \text{K}$ , or  $4.2 \times 10^6 \text{ J m}^{-3} \text{K}$ ). Finally, since the density of air is only approximately 1/1000 that of water, its contribution to the specific heat of the composite soil can be neglected generally.

## Thermal Conductivity of Soils

Thermal conductivity, designated  $\kappa$ , is defined as the quantity of heat transferred through a unit area of the conducting body in unit time under a unit temperature gradient. As shown in Table 2, the thermal conductivities of specific soil constituents differ very markedly (see also Table 3). Hence the space-averaged (macroscopic) thermal conductivity of a soil depends upon its mineral composition and organic matter content, as well as on the volume fractions of water and air.

Since the thermal conductivity of air is very much smaller than that of water or solid matter, a high air content (or low water content) corresponds to a low

thermal conductivity. Moreover, since the proportions of water and air vary continuously,  $\kappa$  is also time-variable. Soil composition is seldom uniform in depth, hence  $\kappa$  is generally a function of depth as well as of time. Unlike heat capacity, thermal conductivity is sensitive not merely to the volume composition of a soil but also to the sizes, shapes, and spatial arrangements of the soil particles.

The relationship between the overall thermal conductivity of a soil and the specific conductivities and volume fractions of the soil's constituents is very intricate, as it involves the internal geometry or structure of the soil matrix and the mode of transmission of heat from particle to particle and from phase to phase.

The dependence of thermal conductivity and diffusivity on soil wetness is illustrated in Figure 1. The influence of latent heat transfer by the diffusion of water vapor in the air-filled pores is proportional to the temperature gradient in these pores. It can be taken into account by adding to the thermal conductivity of air an apparent conductivity due to evaporation, transport, and condensation of water vapor (the so-called vapor-enhancement factor). This value

is strongly temperature-dependent and rises rapidly with increasing temperature.

Because soil water potential depends on temperature, the development of a temperature gradient generally induces the movement of water as well as of heat. Hence techniques for measuring heat transfer through a soil sample based on steady-state heat flow between two planes maintained at a constant temperature differential involve the risk of changing the sample's internal moisture distribution and therefore its thermal properties. During the process of measurement, the soil near the warmer plane becomes drier, while that near the cooler plane becomes wetter. Early attempts to measure thermal conductivity failed to recognize this pitfall as they purported to maintain constant soil moisture conditions during prolonged, steady-state heat flow. Hence their results can only be considered approximations at best. While steady-state methods may be sufficiently accurate for measuring thermal conductivity of dry soils, short-term, transient heat-flow techniques are preferable, in principle, for moist soils.

### Simultaneous Transport of Heat and Moisture

The flows of water and of thermal energy under nonisothermal conditions in the soil are interactive phenomena: the one entails the other. Temperature gradients affect the moisture potential field and induce both liquid and vapor movement. Reciprocally, moisture gradients move water, which carries heat. The simultaneous occurrence of temperature gradients and of moisture potential gradients in the soil therefore brings about the combined transport of heat and moisture.

Two separate approaches to the combined transfer of heat and moisture have been attempted: (1) a

**Table 2** Thermal conductivities of soil constituents (at 10°C) and of ice (at 0°C)

Constituent	$\text{mcal cm}^{-1} \text{ sK}$	$\text{Wm}^{-1} \text{ K}$
Quartz	21	8.8
Other minerals (average)	7	2.9
Organic matter	0.6	0.25
Water (liquid)	1.37	0.57
Ice	5.2	2.2
Air	0.06	0.025

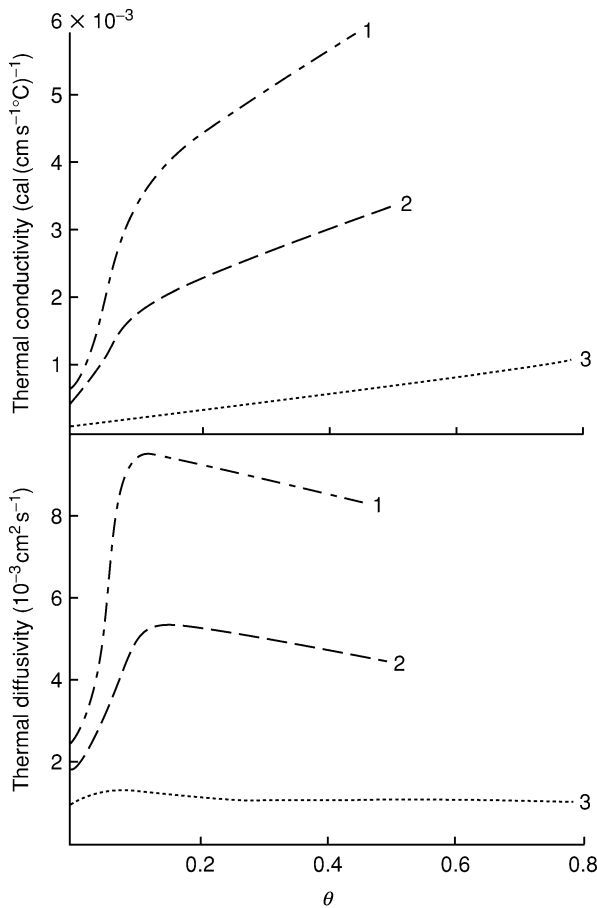
Reproduced with permission from Hillel D (1998) *Environmental Soil Physics*. San Diego, CA: Academic Press.

**Table 3** Average thermal properties of soils and snow<sup>a</sup>

Soil type	Porosity	Volumetric wetness	Thermal conductivity ( $10^{-3} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ } ^\circ\text{C}$ )	Volumetric heat capacity ( $\text{cal cm}^{-1} \text{ s}^{-1} \text{ } ^\circ\text{C}$ )	Damping depth (diurnal) (cm)
Sand	0.4	0.0	0.7	0.3	8.0
	0.4	0.2	4.2	0.5	15.2
	0.4	0.4	5.2	0.7	14.3
Clay	0.4	0.0	0.6	0.3	7.4
	0.4	0.2	2.8	0.5	12.4
	0.4	0.4	3.8	0.7	12.2
Peat	0.8	0.0	0.14	0.35	3.3
	0.8	0.4	0.7	0.75	5.1
	0.8	0.8	1.2	1.15	5.4
Snow	0.95	0.05	0.15	0.05	9.1
	0.8	0.2	0.32	0.2	6.6
	0.5	0.5	1.7	0.5	9.7

<sup>a</sup>After van Wijk and de Vries (1963).

Reproduced with permission from Hillel D (1998) *Environmental Soil Physics*. San Diego, CA: Academic Press.



**Figure 1** Thermal conductivity and thermal diffusivity as functions of volume wetness (volume fraction of water) for: (1) sand (bulk density  $1460 \text{ kg m}^{-3}$ , volume fraction of solids 0.55); (2) loam (bulk density  $1330 \text{ kg m}^{-3}$ , volume fraction of solids 0.5); and (3) peat (volume fraction of solids 0.2). (After de Vries, 1975.) (Reproduced with permission from Hillel D (1998) *Environmental Soil Physics*. San Diego, CA: Academic Press.)

mechanistic approach, based on a physical model of the soil system, and (2) a thermodynamic approach, based on the phenomenology of irreversible processes in terms of coupled forces and fluxes. Though starting from different points of view, the two approaches have been shown to be related and, properly formulated, can be cast into an equivalent mold.

The mechanistic approach is based on the concept of viscous flow of liquid water under the influence of gravity and of capillary and adsorptive forces, and on the concept of vapor movement by diffusion. Local ‘microscopic-scale’ thermodynamic equilibrium between liquid and vapor is assumed to exist at all times and at each point within the soil. The general differential equation describing moisture movement in a porous system under combined temperature and moisture gradients for unidimensional vertical flow is, accordingly:

$$\partial\theta/\partial t = \nabla \cdot (D_T \nabla T) + \nabla \cdot (D_w \nabla \theta) - \partial K/\partial z \quad [14]$$

where  $\theta$  is volumetric wetness,  $t$  time,  $T$  absolute temperature,  $D_T$  the water diffusivity under a temperature gradient (the sum of the liquid and vapor diffusivities),  $D_w$  the water diffusivity under a moisture gradient,  $K$  the hydraulic conductivity, and  $z$  the vertical space coordinate. The last term on the right-hand side is due to the gravity gradient and becomes positive if  $z$  is taken to be increasing downwards.

The heat transfer equation is, similarly:

$$C_v \partial T/\partial t = \nabla \cdot (\kappa \nabla T) - L \nabla \cdot (D_{w,vap} \nabla \theta) \quad [15]$$

Here  $C_v$  is volumetric heat capacity,  $\kappa$  apparent thermal conductivity of the soil,  $L$  latent heat of vaporization of water, and  $D_{w,vap}$  diffusivity for heat conveyed by water movement (mostly vapor). Equations [14] and [15] are of the diffusion type, involving  $\theta$ - and  $T$ -dependent diffusivities as well as gradients of both  $\theta$  and  $T$ .

Taken together, eqns [14] and [15] describe the coupled transport of moisture and heat in soils. The assumption of local thermodynamic equilibrium links the vapor pressure  $p_v$  to the matric potential  $\psi$  by the following relation:  $p_v = p_{vs} h = p_{vs} \exp(Mg\psi/RT)$ , where  $p_{vs}$  is the saturated vapor pressure at the particular temperature  $T$ ,  $h$  relative humidity,  $M$  molar mass,  $g$  acceleration due to gravity, and  $R$  the universal gas constant.

The approach based on the thermodynamics of irreversible processes formulates a pair of phenomenological equations in which the fluxes of moisture  $q_w$  and heat  $q_h$  are expressed as linear functions of the moisture potential (e.g., pressure) gradient  $dp/dz$  and the temperature gradient  $dT/dz$ :

$$\begin{aligned} q_w &= -L_{ww}(1/T)dp/dz - L_{wh}(1/T^2)(dT/dz) \\ q_h &= -L_{hw}(1/T)dp/dz - L_{hh}(1/T^2)(dT/dz) \end{aligned} \quad [16]$$

The four phenomenological coefficients occurring in these equations ( $L_{ww}$ ,  $L_{wh}$ ,  $L_{hw}$ ,  $L_{hh}$ , relating water flow to the water potential gradient, water flow to the thermal potential gradient, heat flow to the water potential gradient, and heat flow to the thermal potential gradient, respectively) are unknown functions of  $p$  (or  $\theta$ ) and  $T$ . According to the Onsager theorem, the cross-coupling coefficients  $L_{wh}$  and  $L_{hw}$  are equal when the fluxes and forces are properly formulated. Thus, the number of coefficients that must be measured is reduced.

An apparent advantage of the irreversible thermodynamics approach is that it makes no *a priori* assumptions regarding the mechanisms of the transport phenomena formulated. Hence it would seem to be less restrictive than a physical theory whose validity

is constrained at the outset by its mechanistic assumptions. The disadvantage of this approach, however, is precisely its failure to address itself to, and provide insight into, the nature and internal workings of the phenomena considered.

## Thermal Regime of Soil Profiles

In nature, soil temperature varies continuously in response to the ever-changing meteorological regime acting on the soil-atmosphere interface. That regime is governed by a regular periodic succession of days and nights, and of summers and winters. Yet the regular diurnal and annual cycles are perturbed by such irregular episodic phenomena as cloudiness, cold waves, heat waves, rainstorms or snowstorms, and periods of drought. Add to these external influences the soil's own changing properties (i.e., temporal changes in reflectivity, heat capacity, and thermal conductivity as the soil alternately wets and dries, and the variation of all these properties with depth), as well as the influences of geographic location, vegetative cover, and, finally human management, and one can expect the thermal regime of soil profiles to be complex indeed.

The simplest mathematical representation of nature's fluctuating thermal regime is to assume that at all depths in the soil the temperature oscillates as a pure harmonic (sinusoidal) function of time around an average value. Assume that, although soil temperature varies differently at different depths in the soil, the average temperature is the same for all depths. A starting time ( $t=0$ ) is chosen such that the surface is at the average temperature. The temperature at the surface can then be expressed as a function of time (Figure 2):

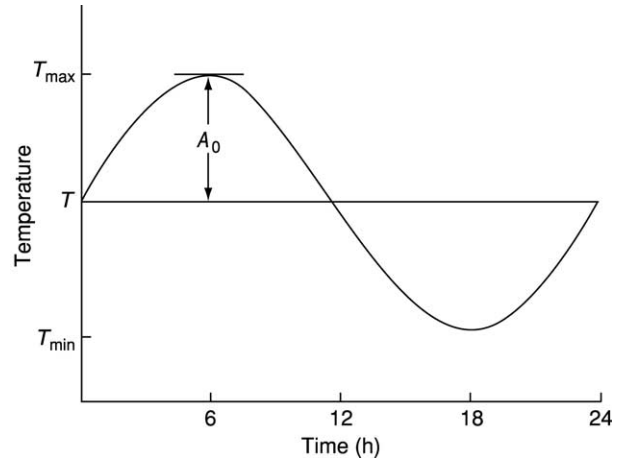
$$T(0, t) = T_{\text{ave}} + A_0 \sin \omega t \quad [17]$$

where  $T(0, t)$  is the temperature at  $z=0$  (the soil surface) as a function of time  $t$ ,  $T_{\text{ave}}$  is the average temperature of the surface (as well as of the profile), and  $A_0$  is the amplitude of the surface temperature fluctuation (the range from maximum, or from minimum, to the average temperature). Finally,  $\omega$  is the radial frequency, which is  $2\pi$  times the actual frequency. In the case of diurnal variation, the period is 86 400 s (24 h), so  $\omega = 2\pi/86\,400 = 7.27 \times 10^{-5} \text{ s}^{-1}$ . Note that the argument of the sine function is expressed in radians rather than in degrees.

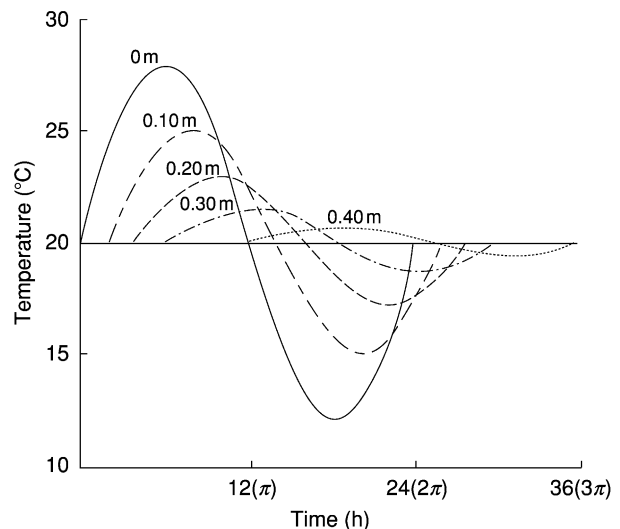
The last equation is the boundary condition for  $z=0$ . For the sake of convenience, let us assume that at infinite depth ( $z=\infty$ ) the temperature is constant and equal to  $T_{\text{ave}}$ . Under these circumstances, the temperature at any depth  $z$  is also a sine function of time, as shown in Figure 3:

$$T(z, t) = T_{\text{ave}} + A_z \sin[\omega t + \phi(z)] \quad [18]$$

in which  $A_z$  is the amplitude at depth  $z$ . Both  $A_z$  and  $\phi(z)$  are functions of  $z$  but not of  $t$ . They can be determined by substituting the solution of eqn [18]



**Figure 2** Idealized daily fluctuation of surface soil temperature, according to the equation:  $T = T_{\text{ave}} + A_0 \sin(\omega t/p)$ , where  $T$  is temperature,  $T_{\text{ave}}$  average temperature,  $A_0$  amplitude,  $t$  time, and  $p$  period of the oscillation (in this case,  $p$  refers to the diurnal 24 h). (Reproduced with permission from Hillel D (1998) *Environmental Soil Physics*. San Diego, CA: Academic Press.)



**Figure 3** Idealized variation of soil temperature with time for various depths. Note that at each succeeding depth the peak temperature is damped and shifted progressively in time. Thus, the peak at a depth of 0.4 m lags about 12 h behind the temperature peak at the surface and is only about 1/16 of the latter. In this hypothetical case, a uniform soil was assumed, with a thermal conductivity of  $1.68 \text{ J m}^{-1} \text{ s}^{-1} \text{ deg}^{-1}$  (or  $4 \times 10^{-3} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ deg}^{-1}$ ) and a volumetric heat capacity of  $2.1 \times 10^6 \text{ J m}^{-3} \text{ deg}^{-1}$  ( $0.5 \text{ cal cm}^{-3} \text{ deg}^{-1}$ ). (Reproduced with permission from Hillel D (1998) *Environmental Soil Physics*. San Diego, CA: Academic Press.)

in the differential equation  $\partial T/\partial t = \kappa(\partial^2 T/\partial z^2)$ . This leads to the solution:

$$T(z, t) = T_{ave} + A_0[\sin(\omega t - z/d)]/e^{z/d} \quad [19]$$

The constant  $d$  is a characteristic depth, called the 'damping depth,' at which the temperature amplitude decreases to the fraction  $1/e$  ( $1/2.718 = 0.37$ ) of the amplitude at the soil surface  $A_0$ . The damping depth is related to the thermal properties of the soil and the frequency of the temperature fluctuation as follows:

$$d = (2\kappa/C\omega)^{1/2} = (2D_h/\omega)^{1/2} \quad [20]$$

At any depth the amplitude of the temperature fluctuation  $A_z$  is smaller than  $A_0$  by a factor  $e^{z/d}$ , and there is a phase shift (i.e., a time delay of the temperature peak) equal to  $-z/d$ . The decrease in amplitude and increase in phase lag with depth are typical phenomena in the propagation of a periodic temperature wave in the soil (Figure 4).

The physical reason for the damping and retarding of the temperature waves with depth is that a certain amount of heat is absorbed or released along the path of heat propagation when the temperature of the conducting soil increases or decreases, respectively. The damping depth is related inversely to the frequency, as can be seen from eqn [20]. Hence it depends directly on the period of the temperature fluctuation considered. The damping depth is  $(365)^{1/2} = 19$  times larger for the annual variation than for the diurnal variation in the same soil.

The annual variation of soil temperature down to considerable depth causes deviations from the

simplistic assumption that the daily average temperature is the same for all depths in the profile. The combined effect of the annual and diurnal variation of soil temperature can be expressed by:

$$T(z, t) = T_{ave,y} + A_y[\sin(\omega_y t + \phi_y - z/d_y)]/e^{z/d_y} + A_d[\sin(\omega_d t + \phi_d - z/d_d)]/e^{z/d_d} \quad [21]$$

where the subscripted indices  $y$  and  $d$  refer to the yearly and daily temperature waves, respectively. Thus  $T_{ave,y}$  is the annual mean temperature. The daily cycles are now seen to be short-term perturbations superimposed upon the annual cycle. Vagaries of weather (e.g., spells of cloudiness or rain) can cause considerable deviations from simple harmonic fluctuations, particularly for the daily cycles. Longer-term climatic irregularities can also affect the annual cycle. The soil temperature profile as it varies seasonally is shown in Figure 4.

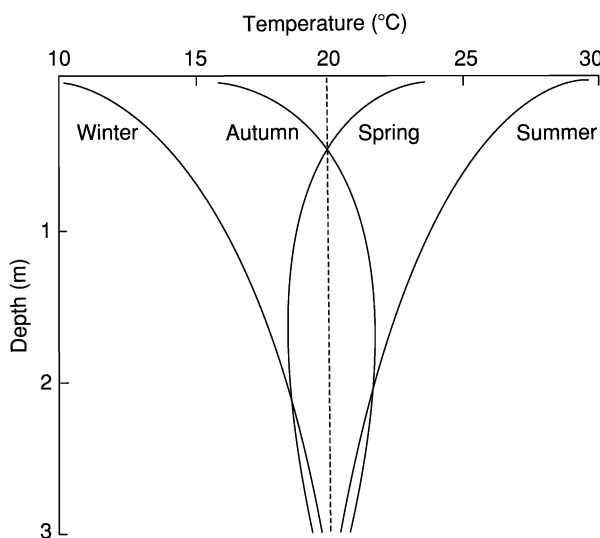
An alternative approach is possible, with fewer constraining assumptions. It is based on numerical rather than analytical methods for solving the differential equations of heat conduction. Mathematical simulation models relying on digital computers now allow soil thermal properties to vary in time and space (e.g., in response to periodic changes in soil wetness), so as to account for alternating surface saturation and desiccation and for profile-layering. They also allow various climatic inputs to follow more realistic and irregular patterns. The surface amplitude of temperature need no longer be taken to be an independent variable, but one that depends on the surface energy balance and thus is affected by both soil properties and above-soil conditions.

Other innovations of practical importance involve the development of techniques for monitoring the soil thermal regime more accurately and precisely than was possible previously. One such technique is the infrared radiation thermometer for scanning or remote sensing of surface temperature for both fallow and vegetated soils without disturbance of the measured surface. Knowledge of the surface temperature and its variation in time is important in assessing energy exchange between the soil and the overlying atmosphere, as well as in determining boundary conditions for within-soil heat transfer.

**See also:** Energy Balance; Evaporation of Water from Bare Soil; Radiation Balance

## Further Reading

Carslaw HS and Jaeger JC (1959) *Conduction of Heat in Solids*. Oxford, UK: Oxford University Press.



**Figure 4** Soil temperature profile as it varies from season to season in a frost-free region. (Reproduced with permission from Hillel D (1998) *Environmental Soil Physics*. San Diego, CA: Academic Press.)

- de Vries DA (1975) Heat transfer in soils. In: de Vries DA and Afgan NH (eds) *Heat and Mass Transfer in the Biosphere*, pp. 5–28. Washington, DC: Scripta Book Co.
- Groenevelt PH and Bolt GH (1969) Non-equilibrium thermodynamics of the soil–water system. *Journal of Hydrology* 7: 358–388.
- Hillel D (1977) *Computer Simulation of Soil–Water Dynamics*. Ottawa, Canada: International Development Research Centre.
- Hillel D (1998) *Environmental Soil Physics*. San Diego, CA: Academic Press.
- Jackson RD and Taylor SA (1986) Heat transfer. In: *Methods of Soil Analysis*. Monograph No. 9, pp. 349–360. Madison, WI: American Society of Agronomy.
- Kutilek M and Nielsen DR (1994) *Soil Hydrology*. Cremin-gen, Germany: Catena-Verlag.
- Philip JR and de Vries DA (1957) Moisture movement in porous materials under temperature gradients. *Transactions of the American Geophysical Union* 38: 222–228.
- van Bavel CHM and Hillel D (1976) Calculating potential and actual evaporation from a bare soil surface by simulation of concurrent flow of water and heat. *Agricultural Meteorology* 17: 453–476.

## THERMODYNAMICS OF SOIL WATER

**P H Groenevelt**, University of Guelph, Guelph, ON, Canada

© 2005, Elsevier Ltd. All Rights Reserved.

### Introduction

The word ‘thermodynamics’ is derived from  $\theta\epsilon\rho\mu\omicron\varsigma$  (heat) and  $\delta\nu\nu\alpha\mu\omicron\varsigma$  (force, power). It presents the science of all forms of energy and mass, including entropic (‘waste’) heat contained in the mass at ambient temperature. The origin of the word suggests that this branch of science deals with both the statics (equilibrium) and the dynamics (nonequilibrium) of energy and mass. Statics (classical thermodynamics) deals with the state of the system in which no heat or mass transfer occurs (this state is extremely rare in natural soils). Dynamics (nonequilibrium thermodynamics) deals with transport processes of mass and heat.

‘Soil water’ is often used interchangeably with the term ‘soil moisture.’ Here we distinguish between the two terms: ‘soil water’ indicating the chemical component  $\text{H}_2\text{O}$  in the soil and ‘soil moisture’ meaning the soil solution. Thermodynamics distinguishes the different chemical components in the system. It deals with the interaction between and transfer of these components and heat.

### Classical (Equilibrium) Thermodynamics of Soil Water

The birth of thermodynamics is rather confusing. The founders tried to deal with such things as the effectiveness of steam engines (S. Carnot). R. Meyer, who was the first (in 1842) to publish the equivalence of work and heat, based his conclusion on his observations of the degree of ‘redness’ of human blood. No

wonder that thermodynamics had a shaky start. The first mathematical formulation of the ‘First Law of Thermodynamics’ (the law of conservation of energy) came from Helmholtz and Joule in 1847. These scientists were dealing with systems that were ‘on the move.’ Yet the system had to be at equilibrium and the ‘changes’ had to be infinitesimally small and ‘reversible’ (meaning that the changes can be reversed without any loss of useful energy at the ambient temperature, or entropy production).

One would expect the First Law of Thermodynamics to equate integral values of the different forms of energy. Yet the equations always come in differential form first. At first only ‘closed’ systems were considered, implying that no mass could move into or out of the system. It was not until J. Willard Gibbs published his two great treatises, *The Equilibrium of Heterogeneous Substances* (in the *Transactions of the Connecticut Academy*, 1876 and 1878), that the ‘system’ was opened up and many of the mysteries of the previous 50 years were clarified. The *Transactions of the Connecticut Academy* were not widely read in Europe, and it was not until C.N. Lewis published his famous book in 1923, 20 years after Gibbs’ death, that Gibbs’ works became widely known. In the year of his retirement, Gibbs remarked that, during the 30 years of his teaching at Yale University, he estimated that only half a dozen of his students had benefited from his lectures.

We start with the integrated Gibbs equation:

$$E = U + \Psi = TS - PV + \sum_i \mu_i m_i + \sum_i \psi m_i \quad [1]$$

where  $E$  is the energy of the system,  $U$  is the ‘internal’ energy, and  $\Psi$  is the energy derived from external force fields.